PATENT SPECIFICATION

803,104

Date of Application and filing Complete Specification April 1, 1957.

No. 10545/57.

Application made in United States of America on April 25, 1956.

Complete Specification Published Oct. 15, 1958.

Index at acceptance:—**Class 32, E2.**

International Classification:—**C10g.**

COMPLETE SPECIFICATION

Process for Cracking Hydrocarbons and a Combination Fluid Solids Reactor and Thermal Cracking Unit

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a combination fluid solids reactor and thermal cracking unit and particularly to an integrated combination designed to obtain high quality products with a minimum of deposition of coke and other objectionable deposits.

In the prior art, processes and apparatus have been developed for carrying out reactions such as conversion of hydrocarbons to lighter products by contacting the feed materials with masses of mobile or "fluidized" solid particles heated to suitably high temperatures. A specific example of such a system is a fluidized solids coking system for conversion of heavy residual hydrocarbon oil.

In the fluidized solids coking system, several difficulties have been encountered. Various solutions have been proposed but have not always been entirely satisfactory. For example, the quality of the gas oil produced in a fluid solids coker, using heavy residual stocks as feed, is not always acceptable as catalytic cracking feed. The gas oil frequently contains heavy ends, high proportions of contaminants which interfere with subsequent cracking operations of sensitive catalyst materials and the like. Moreover, in the overhead outlet system from such cokers, there is a strong tendency to form deposits of carbonaceous residues on the walls and outlet lines of the apparatus. These deposits are extremely objectionable, frequently requiring shutting down of the apparatus for cleaning out and unplugging of clogged lines and removal of accumulated deposits on vessel and internal equipment surfaces, which interfere with the functioning and feed capacity of the system. Various attempts have been made in the past to remedy these problems with varying degrees of success.

The present invention is a process for cracking a heavy residual petroleum stock which comprises contacting the stock with a fluidised bed of hot solid particles to crack and convert at least part of the stock to vapours, the vapours comprising cracked and vapourised stock, removing the vapours from the bed, through a disperse phase above the bed, to a recovery zone where a gas oil is recovered, thermally cracking a feed comprising the gas and passing the hot thermally cracked products into the disperse phase.

A suitable apparatus for carrying out the process comprises the combination of a fluidised solids reactor vessel adapted to contain in its lower portion a bed of hot fluidised solids and in the upper portion of said vessel a disperse phase above the bed, means in said disperse phase in the upper portion of said vessel for separating entrained solid particles from vapors passing upwardly from said disperse phase to return said solid particles to the bed, means for separating a distillate fraction from the vapors produced in the fluidised solid bed, means for passing said distillate fraction through a thermal cracking circuit to thermally crack said distillate fraction and means for reintroducing at least part of the thermally cracked products into said upper portion of said reactor vessel wherein said dispersion phase is contained to add heat thereto and to inhibit formation of carbonaceous deposits therein. The feed to the thermal circuit may be, and preferably is, the gas oil produced in the fluid coker or a part thereof and any unconverted fraction thereof suitable for additional recycle. This feed, if desired, may be supplemented by adding any suitable extraneous feed stock. The gas oil, with or without supplemental stock, is passed through

the thermal cracking circuit. The latter is operated at sufficiently high temperature to accomplish a substantial degree of thermal cracking but the temperature is not high enough to cause substantial conversion to coke or other solid residues. The resulting cracked products from the thermal cracking circuit are introduced into the disperse phase zone above the fluidised solids bed in the reactor. Steam may be introduced along with the thermally cracked vapors, if desired. By this system, substantial heat is added to the disperse phase of the reactor and the vapor pressure of the products normally emerging from the fluidised solids bed is substantially reduced as is the possibility of product condensation on vessel or internal equipment surfaces. The net result is that the products from the solids bed, for example, the conversion products of a coking operation, are carried overhead at higher temperature. Reactions which tend to proceed therein and to cause formation of objectionable carbonaceous deposits are substantially inhibited. Also, by preventing condensation, with consequent deposition of liquid on vessel surfaces, which is a substantial cause of these deposits, is effectively prevented. The degradation which results in the formation of such deposits consequently does not proceed and the apparatus, including the cyclones and outlet lines is kept substantially free from carbonaceous deposits. Also, by the introduction of additional heat into the outgoing vapors, fractionation thereof is facilitated and better separation is obtained between naphtha and gas oil, between gas oil and heavy bottoms. The resulting products are therefore of better quality. The objectionable residues and deposits are minimized in the lighter products, i.e. gas oils up to about 1000—1100° F. end point equivalent to an 80% distillation point in the range of 850—950° F. for the 400° F. plus gas oil. The undesirable heavy fractions are thus concentrated in a bottom fraction which is either withdrawn as such or recycled to the fluid coker system for disposal.

The combination of the thermal cracking circuit to which, for example, the gas oil is subjected for treatment with a fluid solids coker is only one adaptation of the present invention. Another desirable application of this invention is the integration of a thermal cracking circuit, described more fully below, with a conventional fluid catalytic cracking unit. With this type of combination or integration of equipment and process, the products of the thermal cracking circuit are discharged into the dilute phase of the catalytic cracking reactor. This tends not only to reduce coke deposits in the apparatus, which are often encountered, but it will also promote beneficial thermal after-cracking of the vapors emerging from the catalytic cracking bed.

The feed to the thermal cracking circuit may be either the coker gas oil mentioned above, or a combination thereof with other materials such as a cycle gas oil from the catalytic cracker. Alternatively, a catalytic naphtha or even extraneous feeds such as virgin naphtha, light or heavy, may be added. In such a system, there is substantial flexibility in the catalytic cracking operation or in the thermal cracking operation. The ratio of the various feed stocks obviously may be varied considerably in accordance with requirements of the particular refinery and the particular types of feed available thereto.

In the thermal cracking circuit, the gas oil and/or other products to be cracked thermally are passed through suitably heated lines or coils at a temperature which may range from about 950° to 1200° F. or more, at the outlet. Higher temperatures result in greater production of unsaturates and also produce more coke. Hence the maximum permissible temperature depends on the desired type and yields of the various products. In general, temperatures are kept below 1200° F., unless it is desired to produce large quantities of unsaturates and considerable gas and coke. The pressure in this thermal cracking circuit may vary considerably, for example, from 20 to 300 psig. Obviously, the thermal cracking circuit may comprise conventional coils, coil and drum arrangements, and the like. The simple coil circuit is preferred in the present instance. It can be either fired independently in a suitable furnace or fire box or it may comprise a coil immersed in the solids bed of a fluid coker burner, or catalytic unit regenerator. Multiple thermal cracking circuits may be desirable in some cases to permit possible decoking of one circuit while the other is continued in operation.

The major objects of the present invention are to reduce the tendency for coking, i.e. formation of coke deposits, in the overhead and outlet lines of a fluid solids system by releasing thermally cracked products thereto; obtaining economic and processing advantages by combining thermal cracking with other operations, such as coking and/or catalytic cracking, in a fluid bed; and improving the fractionation of the products from a fluid solids system by adding heat thereto in the form of hot vapors of thermally cracked products obtained from a separate thermal circuit.

Reference will now be made to the accompanying drawing which illustrates diagrammatically and in elevation a combination integrated fluid solids and thermal cracking circuit system.

Referring now to the drawing, it will be noted that the major units are a fluidized solids reactor unit 11, a burner or regenerator unit 13 and a furnace 15 containing a thermal cracking circuit or coil system 17.

A heavy residual petroleum stock, is fed to the system through an inlet line 21 and surge drum 23. From the latter, the feed passes

downwardly to a pump 25 through line 27. From the pump 25 the fresh heavy feed passes through line 29 into a fluidized bed of solids, such as finely divided petroleum coke, suitably preheated before coming to the reactor 11. The temperature of the coke particles in the reactor is preferably between about 900° and 1150° F. The feed is distributed suitably through the reactor fluidized coke mass by means of nozzles not shown but well known in the art. The cracked vapourised stock therefrom pass through the interface between the bed and the disperse zone above it as indicated at 31. From here, the vapors pass into a gas-solids separating unit such as cyclone 33 from which the solids are returned preferentially through a dip leg 35, the vapors passing overhead through line 37 into a scrubber unit 39 equipped with suitable baffles 41. The scrubber may or may not be superimposed on the reactor vessel. The scrubbed vapors proceed upwardly past a series of baffles into a fractionating tower 43 preferably directly above the scrubber but may be elsewhere in any suitable position. Here the vapors are fractionated into a gas oil and gases which pass overhead through line 45. A liquid fraction, for example, a gas oil is taken off through line 47 and heavy bottoms are removed through line 49 and pump 51. The latter may be recycled in part to the coking bed through lines 53, 55 and 57, equipped with suitable valves. A portion may be withdrawn as a product through line 59. Preferably, at least a part of the heavy bottoms is recycled through line 61 and heat exchanger 63 to line 65 and back into the scrubber. This material helps to remove entrained heavy ends and solid particles in the scrubber system. If desired, the heat exchanger 63 may be by-passed through a line 67.

A part of the heavy recycle stream may be carried through line 69 into feed line 27 and introduced into the coker with the original or fresh feed for additional processing.

Hot fluidized solids are supplied to or near the top of the reactor fluidized bed by a line 71 which brings them from a burner or regenerator 13. Spent solids from the reactor may be returned through fluid solids transfer line 73 to the burner or regenerator. A portion of the returned solids may be taken from the burner through line 75 to a quench elutriator system 77. Here the coke is sprayed with water, or water plus steam, to cool it and to return the elutriated finer particles back into the burner or regenerator through line 79. The water is supplied through line 81 and the coarser solid particles separated in the quench elutriator may be withdrawn from the system through line 83 to outlet line 85. An air stream may be introduced at line 87 to help remove the coke product.

The above described apparatus is substantially a commercial coking system.

In accordance with the invention, the gas oil stream taken off near the bottom of the fractionation section 43 through line 47 is preferably taken to a surge drum 91, or other equivalent surge facilities. The surge unit is not always necessary but is usually desirable. From here, it is supplied through line 93 to a pump 95 which forces it at suitable pressure, through a line 97 into the thermal cracking circuit 17 operating at about 20—300 psig outlet conditions. Extraneous feed stock, such as gas oil, cycle oil from a catalytic cracker or cracked or virgin naphtha or mixtures thereof may be added to the surge drum through line 99. Vapors from the surge drum may be returned to the coker through line 101. Other side streams may be withdrawn from the fractionator system, if desired. Separate facilities for such withdrawal may be provided through a tower connection suitably located. However, a part of the stream from either of these tower withdrawal connections is preferably recycled through line 105 and pump 107 to line 109, heat exchanger 111 and inlet line 113 to a higher point in the fractionator for heat control and reflux duty. A portion of this recycle material may be fed to the scrubbing section through line 115. Also a portion of the overhead condensed coker naphtha product may be returned to near the tower top for supplementary tower top control duty by means of pump 139 and line 151.

Returning now to the gas oil fraction withdrawn through line 47 to the surge drum 91, this fraction is passed through the thermal cracking circuit. As noted above, the outlet temperature from the thermal cracking coil 17 in furnace 15 should be at least 950° F. and it may be as high as 1200° F. or more. This temperature and the conditions of equipment design and operation should be such, however, as to avoid an objectionable amount of coking in the coil 17.

The thermally cracked gas oil emerges from the furnace through line 121 and passes through one or more lines 123, 125 into the disperse phase at the top of the reactor. The thermally cracked vapors thus introduced into the disperse phase pass upwardly through the cyclone 33 and through its outlet 37 into the scrubber section 39 and the fractionator 43 above it.

Because of their superheating and partial pressure effects, the vapor products of the thermal cracking circuit reduce the tendency toward coking and otherwise forming objectionable deposits in the dilute phase of the reactor. Moreover, the thermally cracked vapors themselves are of improved quality as gasoline blending stocks, giving definite processing and economic advantages. These advantages may be enhanced by introducing catalytic cracking cycle stock and/or virgin light naphtha through line 99 into the feed or surge drum 91 which supplies the thermal cracking circuit. Moreover, as pointed out

above, the added heat supplied to the products emerging from the fluidized solids bed substantially improves fractionation of the overhead products and avoids the inclusion in the final gas oil stream taken from line 47 or 103, of objectionable contaminants such as metal compounds, heavy ends, and the like, which contaminate cracking catalysts with which they may subsequently be contacted.

The gasiform products taken overhead from the fractionator through line 43 are passed through a heat exchanger and/or condenser 131 and thence into a distillate drum 133. From this drum which receives the condensed and cooled products at about 100° F. and at low pressure, preferably within 5 lbs. or so of atmospheric, the condensed steam and other water from the process operations may be withdrawn through outlet line 135. Liquid hydrocarbons in the form of coker naphtha, plus thermal naphtha, are withdrawn as product through line 137 to pump 139 from which they may be passed to suitable storage or further treating facilities through line 141, or returned through line 151 for fractionator tower top control duty. By control of suitable valves, the stream may be divided as desired.

The normally gaseous products, such as hydrogen and C_3 and lighter hydrocarbons, are admixed with some heavier fractions under equilibrium conditions. The mixture is taken overhead from the drum through line 143 for further processing and recovery of desirable fractions as deemed economical.

It will be understood that instead of using the reactor 11 of a fluid coker, a conventional fluid bed catalytic cracking reactor may be employed as the primary base of operations. The operations otherwise may be substantially the same as those described above. In a catalytic cracker of conventional type, the fractionator is not located at the top of the reactor and the products thereof are fractionated. Suitable fractions are obtained, such as the light and heavy naphthas and catalytically cracked gas oil is segregated and withdrawn through conventional facilities. The cycle oil or fraction which is of very refractory nature, may be passed through the subject thermal cracking circuit for conversion. Also, other suitable extraneous feeds as virgin light or heavy naphthas, may be fed and processed through this thermal cracking circuit. The resulting cracked products are discharged to the disperse phase of the fluid catalytic cracking reactor and taken off through the overhead system in the same manner and with the same advantages as previously described. Thus, heavy naphtha, either from virgin distilling operations or from other sources, may be given a thermal treatment to improve its octane number before passing it into the overhead or disperse phase in the primary reactor. This applies to either the coker reactor or the catalytic cracking reactor.

Surge drum 91, or its equivalent, can be inside the fractionating tower if desired. Line 151 may be used for starting up purposes.

WHAT WE CLAIM IS:—

1. A process for cracking a heavy residual petroleum stock which comprises contacting the stock with a fluidised bed of hot solid particles to crack and convert at least a part of the stock to vapours, the vapours comprising cracked and vapourized stock, removing the vapours from the bed, through a disperse phase above the bed, to a recovery zone where a gas oil is recovered thermally cracking a feed comprising the gas oil and passing the hot thermally cracked products into the disperse phase.

2. A process as claimed in Claim 1 in which the solid particles are coke particles.

3. A process as claimed in Claim 1 in which the solid particles are cracking catalyst particles.

4. A process as claimed in any of Claims 1 to 3 in which the oil is a heavy residual oil.

5. A process as claimed in any of Claims 1 to 4 in which the feed which is thermally cracked comprises the liquid product from the recovering zone and a petroleum fraction of lower boiling range than the hydrocarbon oil.

6. A process as claimed in any of Claims 1 to 5 in which the thermal cracking is carried out at 950—1200° F. and a pressure from 20 to 300 p.s.i.g.

7. An apparatus for cracking hydrocarbon oils which comprises the combination of a fluidised solids reactor vessel adapted to contain in its lower portion a bed of hot fluidised solids and in the upper portion of said vessel a disperse phase above the bed, means in said disperse phase in the upper portion of said vessel for separating entrained solid particles from vapours passing upwardly from said disperse phase to return said solid particles to the bed, means for separating a distillate fraction from the vapours produced in the fluidised solid bed, means for passing said distillate fraction through a thermal cracking circuit to thermally crack said distillate fraction and means for re-introducing at least part of the thermally cracked products into said upper portion of said reactor vessel wherein said dispersion phase is contained to add heat thereto and to inhibit formation of carbonaceous deposits therein.

8. An improved process for cracking hydrocarbon oils substantially as hereinbefore described with particular reference to the drawing.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press,—1958.
Published at the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

803,104 COMPLETE SPECIFICATION
1 SHEET
This drawing is a reproduction of the Original on a reduced scale.